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(54) Title: HEAT TREATMENT OF NITROGEN CERAMICS (57) Abstract A method for the production of nitrogen ceramic materials which comprises adding to the starting powdered ceramic material an oxide of a metal which has a boiling point of less than 1700°C, the said metal oxide being included in the mixture in an amount sufficient to densify the material, sintering the powder at a temperature of up to 1800°C and post-sintering the product in a reducing atmosphere under a reduced pressure at a temperature of up to 1700°C, in order to remove the glassy phase from the grain boundaries of the nitrogen ceramic material.		

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HEAT TREATMENT OF NITROGEN CERAMICS

The present invention relates to the vacuum heat treatment of nitrogen ceramic materials, such as silicon nitride and sialon ceramics, in order to remove grain-boundary phase material by volatilization.

Silicon nitride and sialon ceramics are engineering ceramic materials which are characterized by an excellent combination of mechanical properties (stiffness, strength, hardness and toughness); properties which can, in theory, be retained to very high (>1000°C) temperatures.

The sialons are based on compositions containing the elements Si, Al, O, N, hence the acronym. The most successful commercial sialon (β -sialon) has the β -Si₃N₄ crystal structure, but with some of the silicon atoms replaced by aluminium atoms and the same number of nitrogen atoms replaced by oxygen atoms to give a general composition of the type Si_{6-2Z}Al_{2Z}O_ZN_{8-2Z} where $0 < Z < 4.2$. The other common sialon phases are O-sialon, which has the general composition Si_{2-X}Al_XO_{1+X}N_{2-X}, where $0 < X < 0.20$ and α -sialon, which has the general composition M_XSi_{12-m-n}Al_{m+n}O_nN_{16-n}, where m represents the number of Si-N bonds replaced by Al-N per unit cell, n represents the number of Si-N bonds replaced by Al-O per unit cell, $0 < X < 2$, and M is one of the cations Li, Mg, Ca, Y and rare earths (excluding La, Ce). O-Sialon has an expanded silicon oxynitride (Si₂N₂O) crystal structure and α -sialon has an expanded α -Si₃N₄ crystal structure.

β -Sialon is a strong engineering ceramic with good oxidation resistance and creep resistance up to 1300°C. The O-sialon has approximately two thirds the strength of β -sialon, but has very much

improved oxidation resistance up to 1400°C.

α -Sialon has excellent hardness, but slightly worse strength, toughness and oxidation resistance than the other two sialons. By selecting a particular phase (or combination of two phases) it is clearly possible to define quite precisely an optimum combination of mechanical properties. Combinations of α - β and O- β sialons are in thermodynamic equilibrium and so optimized composite materials can be produced in this way.

Sialons are usually formed by mixing Si_3N_4 , Al_2O_3 , AlN powders with one or more metal oxides (often including Y_2O_3), compacting the powder to the desired shape, and then firing the component at 1750°C for a few hours. The function of the metal oxide is to react with the silica (which is always present on the surface of each silicon nitride particle) and the alumina (which is always present on the surface of each aluminium nitride particle), to form a liquid phase which dissolves the reactants and precipitates the product. The liquid phase (which still contains dissolved nitrogen), cools to form a glass between the sialon grains. In subsequent use of these materials the glass starts to soften at temperatures slightly above the glass transition temperature (T_g) and the mechanical properties deteriorate rapidly. Even with the most refractory oxide additives, T_g is barely in excess of 1000°C. Heat treatment of this glass can convert the glass into a mixture of crystalline phases, and the refractories of the product is then determined by the lowest eutectic temperature in the system (typically 1300-1400°C in most M-Si-Al-O-N systems). The grain boundary phase is a necessary evil in these materials, being a remnant of the densification process. Typically, a Y_2O_3 densified β -sialon

contains about 15 volume percent of Y-Si-Al-O-N glass and 85 volume percent β -sialon. At temperatures above $\sim 950^{\circ}\text{C}$ this glass begins to soften and the strength decreases. The material can be heat treated at $\sim 1300^{\circ}\text{C}$ to crystallise the glass. In the case of β -sialon containing Y-Si-Al-O-N glass, the glass crystallises to give $\text{Y}_3\text{Al}_5\text{O}_{12}$ (yttrio garnet or YAG) and a small amount of additional β -sialon. This crystallisation process reduces the room temperature strength of the material, but this reduced strength is maintained to higher temperature. The reason that crystallisation reduces strength is not completely understood, but is probably because the crystalline YAG occupies a smaller volume than the glass it replaces; crystallisation therefore leaves small pores within the microstructure.

With O-sialon - glass the crystallisation of the glass produces $\text{Y}_2\text{Si}_2\text{O}_7$ (yttrium disilicate) plus a small amount of additional O-sialon. α -Sialons incorporate the sintering additive into the crystal lattice, and original studies tried to simultaneously achieve densification and α -sialon formation. However, so far it has been impossible to produce a 100% α -sialon material which does not contain either residual porosity or residual glass.

We have now developed a method for the preparation of densified nitrogen ceramic materials which have improved high temperature properties, together with a significantly reduced amount of the grain boundary phase material.

Accordingly, the present invention provides a method for the production of nitrogen ceramic materials which comprises adding to the starting powdered ceramic material an oxide of a metal which has a boiling point of less than 1700°C , or a mixture of such oxides, sintering the powder at a

temperature of up to 1800°C and post-sintering the product in a reducing atmosphere under a reduced pressure at a temperature of up to 1700°C, the said metal oxide being included in the mixture in an amount sufficient to densify the material and then to remove the glassy phase from the grain boundaries of the nitrogen ceramic material.

The method of the present invention enables dense, refractory, silicon nitride and sialon ceramics to be produced which have good chemical and mechanical properties which are retained to significantly higher temperatures than current commercial materials which, because they contain M-Si-O-N or M-Si-Al-O-N glassy or crystalline boundary phases, fail at temperatures below 1400°C.

The method of the present invention also enables essentially pure, fully dense α -sialon, β -sialon, O-sialon and β -silicon nitride to be produced which materials could not previously be prepared by the methods known in the art. Thus, although silicon nitride produced by chemical vapour deposition is essentially pure it is always α -Si₃N₄ and it is not possible to produce β -Si₃N₄ by this route. Other routes for the preparation of silicon nitride have an additional grain boundary phase and thus are not essentially pure. In carrying out the method of the present invention the metal oxide having a boiling point of less than 1700°C, which is added to the powdered ceramic starting material, is totally removed.

Accordingly, the present invention includes within its scope an essentially pure, fully dense β -sialon, O-sialon or β -silicon nitride which has a density of at least 98.0% and a purity of above 99% of the theoretical. This material has substantially no grain boundary phase material therein.

In particular, the invention includes within its scope an essentially pure, fully dense β -sialon or O-sialon containing substantially only silicon, aluminium, oxygen and nitrogen which has a density of at least 99.5% and a purity of above 99% of the theoretical.

The invention also includes within its scope an essentially pure, fully dense β -silicon nitride containing substantially only silicon and nitrogen which has a density of at least 98.5% and a purity of substantially 100% of the theoretical.

The invention further includes within its scope an essentially pure, fully dense mixture of α -sialon and β -sialon comprising from 5 to 99% by weight of β -sialon which has a density of at least 98% and a purity of at least 99% of the theoretical.

The invention still further includes within its scope essentially pure, fully dense mixture of β -sialon and O-sialon comprising from 5 to 99% by weight of β -sialon which has a density of at least 98% and a purity of at least 99% of the theoretical.

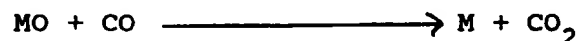
The amount of β -sialon in the above mixed compositions is preferably in the range of from 40 to 60% by weight.

The preferred nitrogen ceramic materials used in the method of the present invention are silicon nitride, α , β or O-sialon, or mixtures thereof.

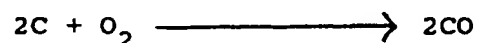
The metal oxide is preferably Li_2O , MgO or SrO , these metals having boiling points of 1324° , 1100° and 1381°C , respectively. Less preferred metal oxides for use in the invention are Na_2O , CaO or Yb_2O_3 these metals having boiling points of 882° , 1484° and 1194°C , respectively.

The reducing atmosphere under which the reduced

pressure post-sintering is carried out is preferably provided by using a carbon resistance furnace. When a carbon resistance furnace is used the reducing species is carbon monoxide and the reaction proceeds according to the following equation:



where M represents any metal species which has a boiling point of less than 1700°C. The carbon dioxide then reacts with hot graphite components in the furnace to produce further carbon monoxide. The carbon environment also reduces the partial pressure of oxygen in the gas atmosphere to that specified by the equilibrium



at the temperature used. The removal of the oxide rich species by a reducing medium proceeds more effectively at a reduced partial pressure of oxygen.

The reduced pressure post-sintering is preferably carried out by placing the sample in a carbon crucible and surrounding the sample with a packing bed of powdered carbon or powdered boron nitride, the packing material preventing the formation of SiC by reaction between Si_3N_4 and C above 1600°C and preventing the loss of volatiles from the outside of the samples.

The metal oxide, MO, is generally added to the nitrogen ceramic material in the minimum amount needed for densification. When MgO is used as the additive it is generally added in an amount of less than 2% by weight and preferably less than 1% by weight. It is beneficial to use the minimum amount of additive (consistent with achieving full density), because after the reduced pressure heat treatment

there is some residual porosity, and the less grain boundary glass, the smaller is the residual porosity.

The mixture of the starting powder and metal oxide is preferably hot pressed, pressureless sintered, gas pressure sintered or hot-isostatically pressed to form a dense sample prior to the reduced pressure heat treatment. Hot pressing is the preferred technique for silicon nitride ceramic materials and pressureless sintering for sialon materials.

The reduced pressure post-sintering step is preferably carried out under a partial vacuum, and more preferably under a partial vacuum pressure of 10^{-1} atmospheres, or below, which may be achieved, for example, by the use of a rotary pump.

The method of the present invention provides silicon nitride and sialon ceramics with improved high temperature properties, such as creep resistance, oxidation resistance and hot hardness. The reduced pressure treatment may result in some decrease in strength and also some reduction in toughness, but at acceptable levels. Furthermore, the hot hardness of the material is good and it is anticipated that the materials retain about 50% of their room temperature hardness at 1400°C .

The present invention will be further described with reference to Figures 1 to 5 of the accompanying drawings.

Figure 1 is a graph showing the creep behaviour of a 1% MgO hot pressed typical commercial silicon nitride (containing a high level of iron impurities) in which trace (a) shows the creep resistance for a sample as received, trace (b) shows the creep resistance for a sample after heat treatment at 1250°C and trace (c) shows the creep resistance for a sample after vacuum heat treatment at 1600°C for 4 hours. The improvement in the creep resistance of the

vacuum heat treated sample is significant.

Figure 2 is a graph illustrating the microhardness of silicon nitride as a function of the MgO additive content. The two zero additive points correspond to the 1% and 2% MgO materials after vacuum heat treatment. The vacuum heat treatment results in a significant increase in microhardness.

Figure 3 shows the EDX analyses of sintered and vacuum heat treated 1% MgO densified β -sialon as (a) hot-pressed and (b) after 3 hours vacuum heat treatment at 1625°C.

Figure 4 shows the EDX analyses of sintered and vacuum heat treated 2.8% CaO densified β -sialon as (a) hot-pressed and (b) after 3 hours vacuum heat treatment at 1575°C.

Figure 5 shows the EDX analyses of sintered and vacuum heat treated 2% MgO densified β -silicon nitride (a) hot-pressed and (b) after 3 hours vacuum heat treatment.

Figures 3, 4 and 5 show that the metals are lost from the samples on vacuum heat treatment.

The present invention will be further described with reference to the following Examples in which parts and percentages are by weight, unless otherwise stated.

Examples 1 to 9

Magnesium oxide was added in amounts of 1% or 2% by weight to silicon nitride or β -sialon and the mixture hot pressed or pressureless sintered, respectively. A sample of the pressed mixture 5mm in thickness was placed in a carbon crucible and surrounded with a packing bed of boron nitride. The mixture was then heat treated at a temperature of 1575°C for silicon nitride, or 1625°C for

β -sialon, in a carbon resistance furnace under a vacuum of 10^{-1} atmospheres for periods of time of 1, 2 or 3 hours. The results are given in Table 1 below. For comparative purposes the procedure was repeated using an addition of 2.8% CaO to silicon nitride and the pressed mixture fired at 1575°C . The results are also given in Table 1.

In compiling the results in Table 1 the % theoretical density (TD) has been calculated using an assumption of the theoretical density of $\beta\text{-Si}_3\text{N}_4$ of 3.195 g/cm^3 and of the theoretical density of β -sialon of 3.155 g/cm^3 .

Table 1

Example No.	Type of Material	Heat Treatment Temp °C	Time h	Weight Loss %	Density gcm ⁻³	Theoretical %	X-ray Result Phases
1	2% MgO SN	1575°	1	4.20	3.162	98.97	β -Si ₃ N ₄
2	2% MgO SN	1575°	2	5.20	3.152	98.65	β -Si ₃ N ₄
3	2% MgO SN	1575°	3	5.75	3.146	98.47	β -Si ₃ N ₄
4	1% MgO SN	1575°	1	2.20	3.158	98.84	β -Si ₃ N ₄
5	1% MgO SN	1575°	2	2.65	3.152	98.65	β -Si ₃ N ₄
6	1% MgO SN	1575°	3	2.90	3.145	98.44	β -Si ₃ N ₄
7	1% MgO β	1625°	1	2.60	3.181	100.00	β -sialon
8	1% MgO β	1625°	2	3.25	3.181	100.00	β -sialon
9	1% MgO β	1625°	3	3.75	3.171	100.00	β -sialon
Comparative	2.8% CaO SN	1575°	3	5.25	2.853	89.30	β -Si ₃ N ₄

The hardness and fracture toughness data for the materials of Examples 3 and 9 are given in Table 2 below. These are compared to the values obtained for sintered materials of the same formulation which have not been vacuum heat treated (VHT).

Table 2

Example No.	Treatment	Hv (Kg/mm ²) 10 Kg Load	K _C (MPam ^{1/2}) 10 Kg Load
3	As sintered	1435	7.09
3	VHT	1720	5.45
9	As sintered	1555	7.40
9	VHT	1684	5.60

Example 10

Oxidation resistance tests were performed at 1250^o, 1400^o and 1650^oC for 24 hours in air for samples of β -sialon and hot pressed silicon nitride which, with the addition of 1% by weight of MgO, had been subjected to vacuum heat treatment in accordance with the present invention. The results were compared with the oxidation resistance at the same temperatures for samples of a commercial 201 SYALON material.

At 1250^oC there was no weight gain in any of the samples. At 1400^oC the commercial 201 SYALON material had oxidised significantly, whereas the vacuum heat treated β -sialon was just beginning to develop a glassy coating. At 1650^oC the commercial 201 SYALON material was totally degraded whilst the vacuum heat treated hot-pressed silicon nitride material showed little degradation.

Examples 11 to 22

Various additives were incorporated into silicon nitride or β -Sialon and the mixture hot pressed or pressureless sintered respectively. A sample of the mixture 5mm in thickness was placed in a carbon crucible and surrounded with a packing bed of carbon powder. The mixture was then heated treated at the temperature and for the period of time given in Table 3 in a carbon resistance furnace under a vacuum of 10^{-1} atmospheres.

In compiling the results in Table 3 the % theoretical density (TD) has been calculated using an assumption of the theoretical density of β - Si_3N_4 of 3.195 g/cm^3 and of the theoretical density of β -sialon of 3.155 g/cm^3 .

Table 3

Example No.	Additive	Material	Density (g/cm ³)	VHT Temp (°C)	VHT Time (h)	Weight Loss (%)	Density (g/cm ³)	% TD	X-Ray Results
11	2% MgO	Si ₃ N ₄	3.21	1575	2	6.1	3.14	98.3	β -Si ₃ N ₄
12	1% MgO	Si ₃ N ₄	3.18	1575	2	4.7	3.14	98.3	β -Si ₃ N ₄
13	0.5% MgO	Si ₃ N ₄	3.18	1575	2	3.9	3.15	98.6	β -Si ₃ N ₄
14	1% MgO z=1	Sialon	3.18	1625	2	4.3	3.13	99.2	β -sialon
15	0.5% MgO z=1	Sialon	3.18	1625	2	3.9	3.14	99.5	β -sialon
16	0.25% MgO z=1	Sialon	3.17	1625	2	3.2	3.14	99.5	α -Si ₃ N ₄ / β -sialon
17	1% MgO z=0.25	Sialon	3.15	1625	2	4.47	3.12	98.9	α -Si ₃ N ₄ / β -sialon
18	1.5% Li ₂ O	Si ₃ N ₄	3.03	1450	1/2	7.45	2.95	92.3	α -Si ₃ N ₄
19	0.75% Li ₂ O z=1	Sialon	3.09	1550	1	5.6	3.00	95.1	β -sialon
20	5.18% SrO	Si ₃ N ₄	3.23	1625	2	8.3	3.14	98.3	β -Si ₃ N ₄
21	2.59% SrO z=1	Sialon	3.26	1650	2	7.2	3.18	100.0	β -sialon
22	3% Y ₂ O ₃ /5.22%Yb ₂ O ₃	Sialon	3.36	1650	2	6.7	3.27	100.0	α - β -sialon

CLAIMS:

1. A method for the production of nitrogen ceramic materials which comprises adding to the starting powdered ceramic material an oxide of a metal which has a boiling point of less than 1700°C , or a mixture of such oxides, sintering the powder at a temperature of up to 1800°C and post-sintering the product in a reducing atmosphere under a reduced pressure at a temperature of up to 1700°C , the said metal oxide being included in the mixture in an amount sufficient to densify the material and then to remove the glassy phase from the grain boundaries of the nitrogen ceramic material.
2. A method as claimed in claim 1 wherein the metal oxide is Li_2O , MgO or SrO .
3. A method as claimed in claim 1 or claim 2 wherein the metal oxide is MgO and is added to the ceramic material in an amount of up to 2% by weight.
4. A method as claimed in any one of the preceding claims wherein the ceramic material is β -silicon nitride, α -sialon, β -sialon, O-sialon, or mixtures thereof.
5. A method as claimed in any one of the preceding claims wherein the mixture of the ceramic material and metal oxide is hot pressed or pressureless sintered prior to the post-sintering treatment under reduced pressure.
6. A method as claimed in any one of the preceding claims wherein the post-sintering treatment is carried out under a reduced pressure of 10^{-1}

atmospheres or below.

7. A method as claimed in any one of the preceding claims wherein the reducing atmosphere is provided by a carbon resistance furnace.

8. A method as claimed in any one of the preceding claims wherein the sintered ceramic material is surrounded by a packing bed for the post-sintering treatment under reduced pressure.

9. A method as claimed in claim 8 wherein the packing bed is powdered boron nitride or powdered carbon.

10. An essentially pure, fully dense β -sialon, O-sialon or β -silicon nitride containing substantially no grain boundary phase material which has a density of at least 98.0% and a purity of above 99% of the theoretical.

11. An essentially pure, fully dense β -sialon or O-sialon containing substantially only silicon, aluminium, oxygen and nitrogen, which has a density of at least 99.5% and a purity of about 99% of the theoretical.

12. An essentially pure, fully dense β -silicon nitride containing substantially only silicon and nitrogen which has a density of at least 98.5% and a purity of substantially 100% of the theoretical.

13. An essentially pure, fully dense mixture of α -sialon and β -sialon comprising from 5 to 99% by weight of β -sialon which has a density of at

least 98% and a purity of at least 99% of the theoretical.

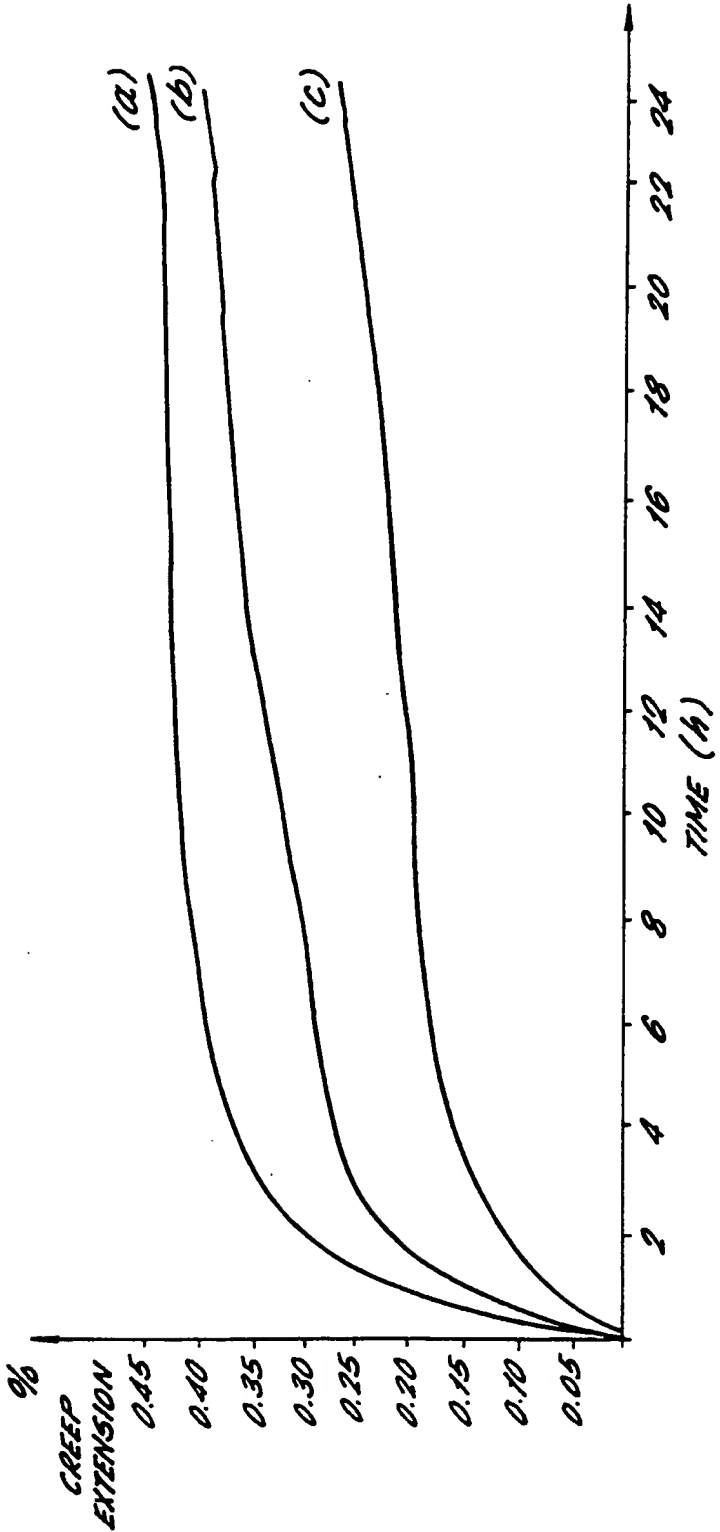
14. A mixture of α -sialon and β -sialon as claimed in claim 13 which comprises from 40 to 60% by weight of β -sialon.

15. An essentially pure, fully dense mixture of β -sialon and O-sialon comprising from 5 to 99% by weight of β -sialon which has a density of at least 98% and a purity of at least 99% of the theoretical.

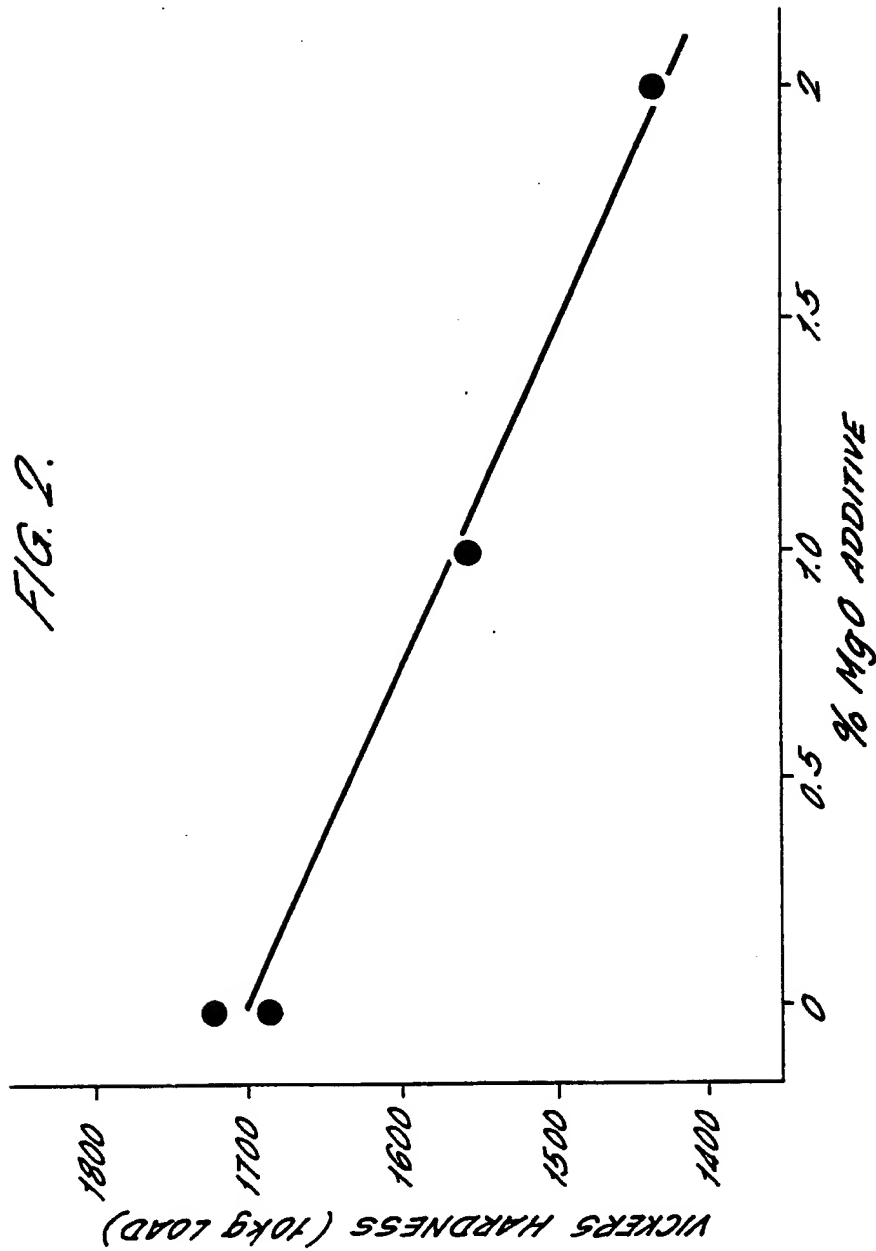
16. A mixture of β -sialon and O-sialon as claimed in claim 15 which comprises from 40 to 60% by weight of β -sialon.

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FIG. 1.



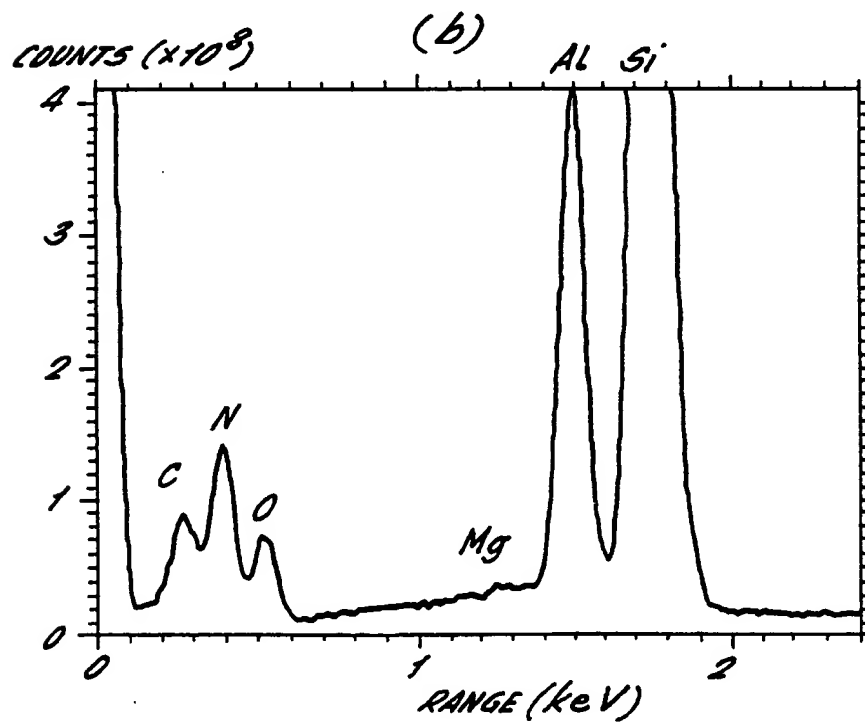
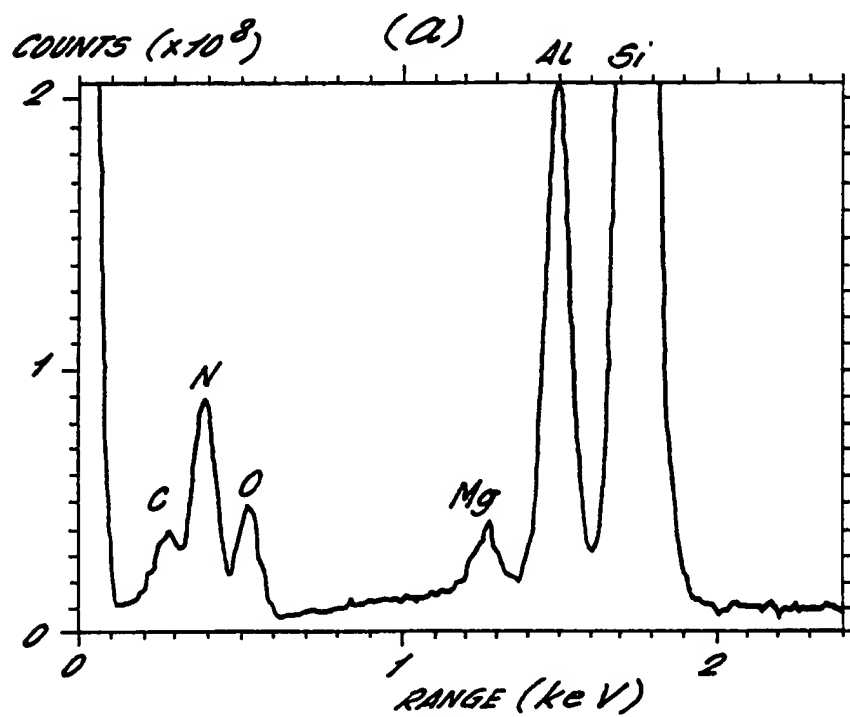
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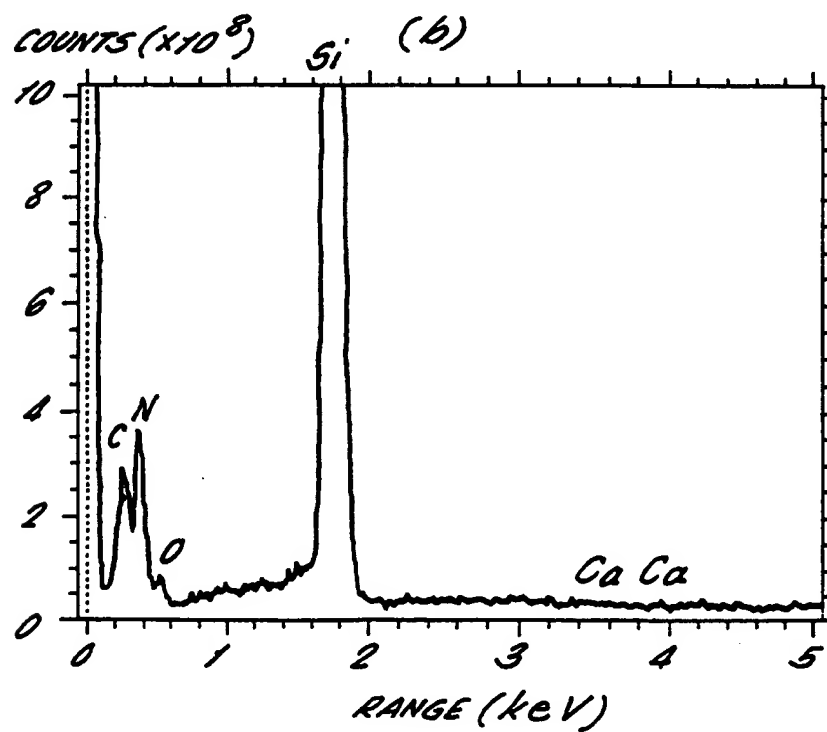
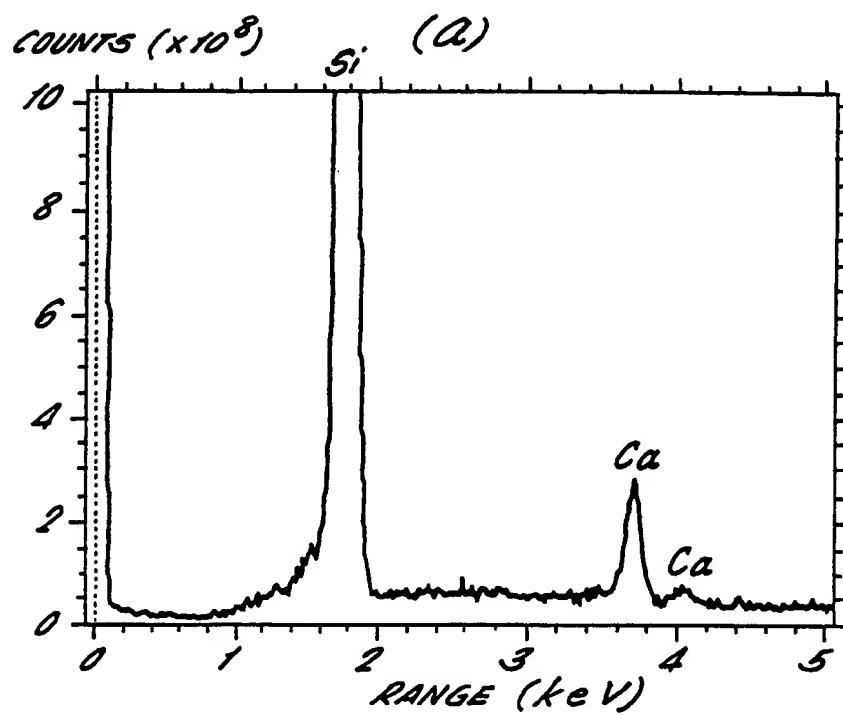


SUBSTITUTE SHEET

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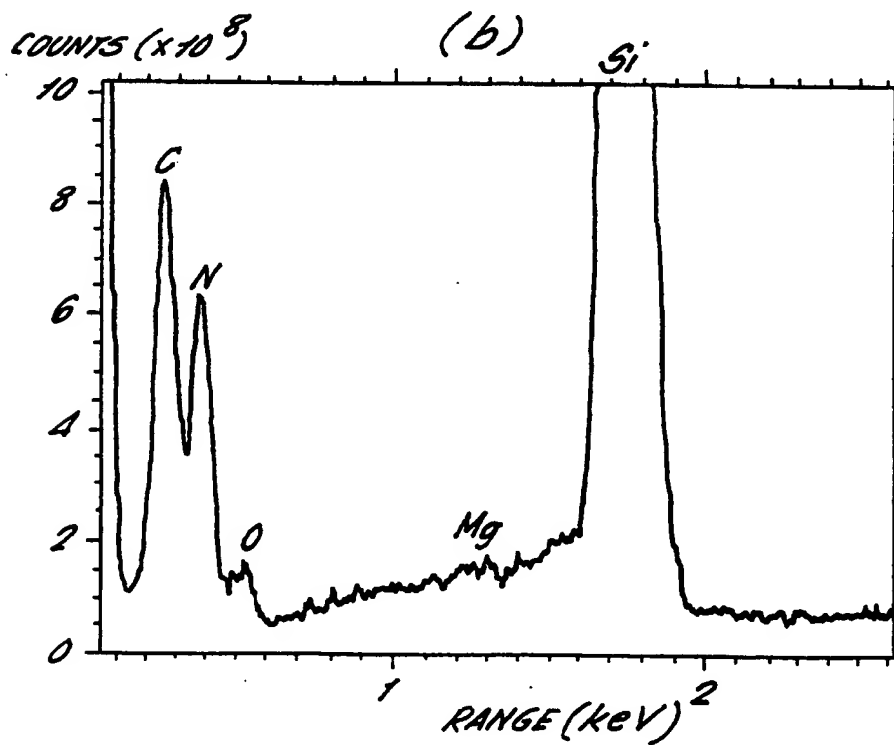
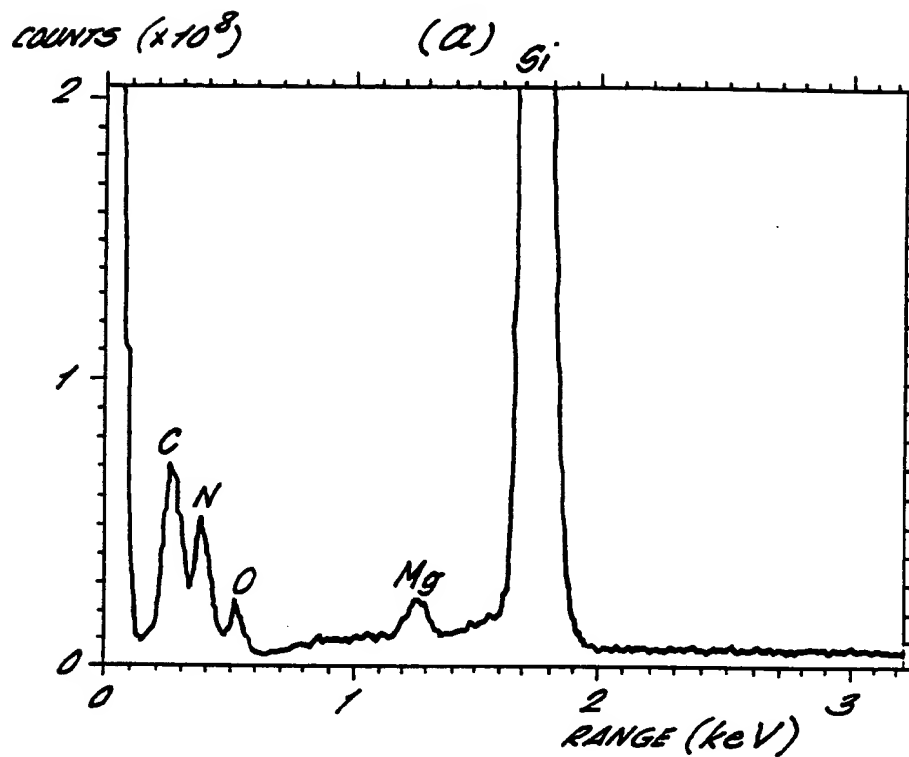
FIG. 3.



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FIG. 4.

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FIG. 5.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 93/02032

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 5 C04B35/58 C04B41/53

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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IPC 5 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US,A,4 376 742 (T.-I. MAH) 15 March 1983 see column 3, line 26 - line 35; claims 1-5 ---	10,12 1-9
X	US,A,4 623 498 (E.C. BECKWITH ET AL.) 18 November 1986 see column 5, line 9 - line 12; claim 1 see column 6, line 9 - line 23 ---	10,12
X	US,A,5 032 553 (C.A. TARRY) 16 July 1991 see table 1 ---	10,11, 13,14
X	EP,A,0 344 642 (GOVERNMENT INDUSTRIAL RESEARCH INSTITUTE ET AL.) 6 December 1989 see column 7, line 2 - line 4; claims 1,3,4; examples 2-4 -----	10,11, 15,16

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Information on patent family members

national Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4376742	15-03-83	NONE	
US-A-4623498	18-11-86	CA-A- 1221527	12-05-87
US-A-5032553	16-07-91	NONE	
EP-A-0344642	06-12-89	JP-A- 1301565	05-12-89
		US-A- 4935389	19-06-90